INFLUENCE OF TEMPERATURE ON THE INFRARED SPECTRUM OF THE CORONENE MOLECULE

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ABSTRACT

Laboratory experiments were done to investigate the temperature dependence of the absorption spectrum of the coronene ($C_{24}H_{12}$) molecule in the infra-red. Because of it's compactness, the coronene is believed to be typical of the interstellar medium (ISM) polycyclic aromatic hydrocarbons (PAHs) population (see ref. 1).

The main result is that the spectrum is temperature independent in the explored range, supporting the modelisation of the astronomical infrared bands with emission from PAHs.

In the fine structure of the spectrum, very small temperature correlated fluctuations are observed which are not detected with actual photometric means in the interstellar medium. Qualitative arguments are given to investigate wether this structure is due to coronene or laboratory experiment artefacts.

LABORATORY EXPERIMENT RELEVANCE

In the ISM, the emitted intensity is $I_\lambda(T) = \varepsilon_\lambda(T).B_\lambda(T)$

where
- $\varepsilon_\lambda(T)$ is the emissivity
- $B_\lambda(T)$ is the Planck function.

In the laboratory, it is easier to take absorption spectra. One measures, for an optically thin sample, the absorptivity :

$$A_\lambda(T) = \frac{J_0 - J_\lambda}{J_0} = 1 - e^{-N\sigma_\lambda(T)} \approx N\sigma_\lambda(T)$$

where
- J_0 and J_λ are the incident and transmitted intensities respectively
- N the column density of the molecule in the sample
- σ_λ the absorption cross section.

From Kirchhoff's law, one can compute the emitted spectrum at the temperature T, knowing $A_\lambda(T)$:

$$I_\lambda(T) = B_\lambda(T) \, A_\lambda(T)$$

which is in agreement with the observed spectra assuming that $A_\lambda(T)$ is mostly independent of the temperature.

With the increase in temperature, the population of the vibrational levels is suspected to change : upper levels (v=2, 3, ...) can be populated and thus, emission from these upper levels is expected (v=1→2, v=2→3, ...)

So, IR bands emitters identification is partly based upon temperature independence of the PAHs spectra which are usually known at room temperature.

EXPERIMENTAL TECHNIQUES

Spectra were recorded in solid phase. This technique had to be used because coronene is a solid up to 470 K so that gaseous phase spectra cannot easily be obtained at intermediate temperatures and require otherwise long path cells for sufficient absorption.

pellets :

Coronene was mechanically mixed in C_sI (to obtain an optical depth $\tau \approx 1$ at 3.3 μm) and pressed to make a pellet.
In the same conditions, we made a blank pellet (without coronene), which spectrum is used as reference to subtract the C_sI component.
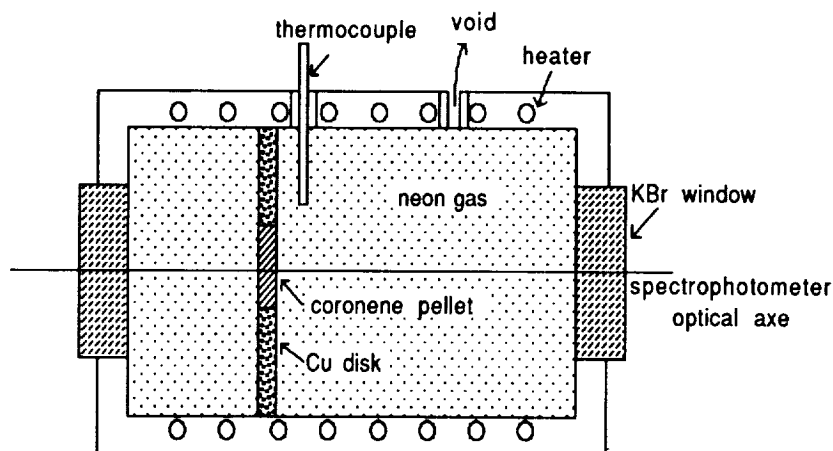
cell :

figure n°1 : Schematical view of the warmed cell used to obtain spectra at high temperatures(300-492 K). C_u disk and neon gas ensure a good thermal equilibrium between the heater and the coronene pellet. KB_r is used for the windows because of its transparancy in the IR. Temperature is measured with a thermocouple with an accuracy better than ≈1 K.

We used the warmed cell shown in fig. n°1. The pellet is fixed on a C_u disk and the cell is filled with 10 mbar of an inert gas (neon) to ensure a good thermal equilibrium between the cell and the pellet. Windows are made of KB_r which is transparent in the IR and the temperature is measured by a thermocouple.

Spectrophotometer :
Fourrier transform spectrophotometer of the BOMEM DA3 series.

Experimental parameters :
-Explored range of temperature : 300 K-500 K known with an accuracy better than ΔT=1K.

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-Frequency range : between 400 and 4000 cm^{-1} (25 μm and 2,5 μm) with a Δv=1 cm^{-1} spectral resolution.

RESULTS

Coronene evaporation from the pellet was not detected. For temperatures higher than 500 K, we were limited by coronene evaporation from C$_s$I matrix. Contamination by residual CO_2 or H_2O is identified in their strong IR activity regions (around 1600 cm^{-1} for H_2O and 670 cm^{-1} for CO_2) and contamination is find to be weak near the features of interest.
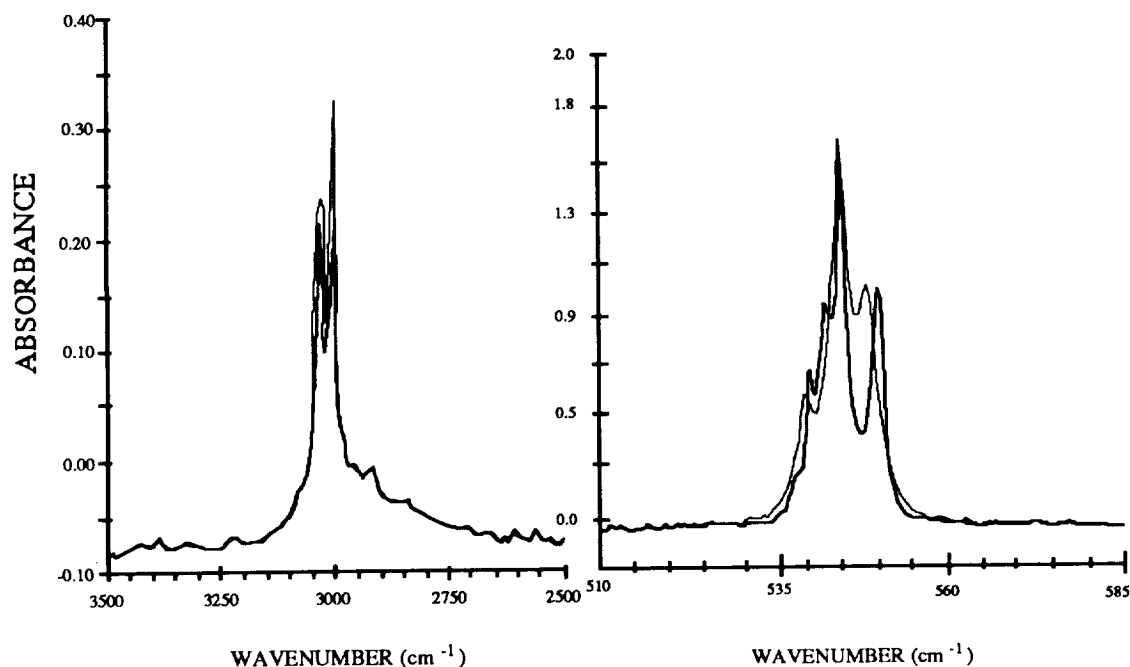

figure n°2: spectra at two extreme temperatures for the 3.3 μm and 18 μm lines.
bold line : spectrum at 298 K
normal line : spectrum at 497 K

Two typical bands are shown on fig. n°2 for different values of the temperature.

In fig. n°3, we have shown the values of the integrated intensities over the emission line and λ_{gc} the line gravity center.

These quantities appear to be constant if one accepts an error of 6,3% and 2,3% for I and λ_{gc} respectively. The error at 3.3 μm is larger because of the incertitude on the baseline due to the shape of the continuum at this wavelength neighborhood.

So, we can conclude that the shape of the spectrum for the coronene between 400 and 4000 cm^{-1} is not sharply temperature dependent in the range 300 K - 500 K.

integrated absorbance		Log (λ_{gc}) cm^{-1}	
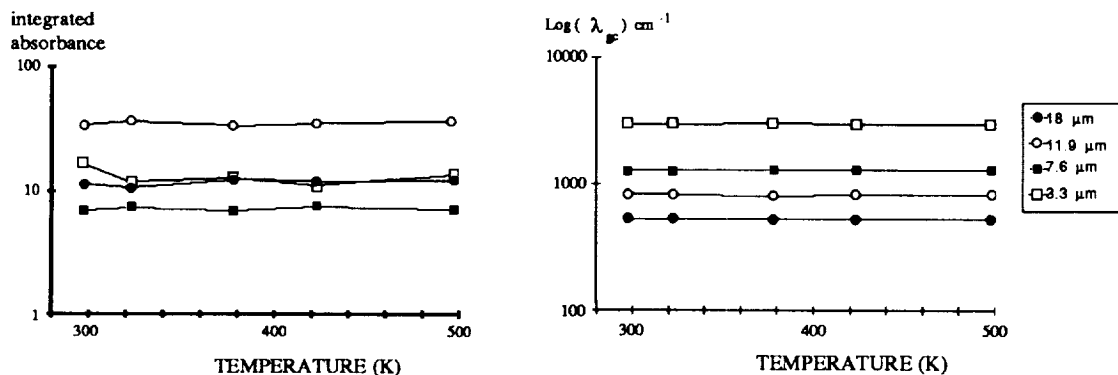
figure n°3 : results of the experiment showing that coronene absorptivity is temperature independent.

- Integrated absorbance for each strong IR absorption line of the coronene spectrum between 400 and 4000 cm^{-1} versus temperature between room temperature and 492 K. Units are arbitrary. These intensities are constant over the explored range of temperature at a 6.3%, 1.4%, 1.8%, 2.5% level for 3.3, 7.6, 11.9 and 18 μm respectively.

- same graphic for λ_{gc} the gravity center of each line in logarithmic scale. Errors are smaller than : 1.7%, 0.1%, 2.3 %, 0.4% for 3.3, 7.6, 11.9 and 18 μm respectively.

IDENTIFICATION OF THE FINE STRUCTURE

Each strong absorption line in the spectrum presents the aspect of fig. n°2. It is composed of several lines ($\approx$ 5 cm^{-1} and $\approx$ 55 cm^{-1} distant from each other at 11.8 and 3.3 μm respectively). Each individual line of the group is broadened when the temperature is increased. The same behavior is observed for each strong absorption line in the spectrum of the coronene.

We can try to explain the existence of such a fine structure by two different processes :

- An intramolecular one : Fermi coupling with harmonics or mode combinations
- An extra-molecular process : dipole-dipole interaction between coronene molecules.

FERMI COUPLING

The 102 natural modes of the coronene molecule can be grouped under the 12 symmetry types of the D$_{6h}$ symmetry group. The IR active ones are in good agreement with the principal features of the laboratory spectra.

Due to the anharmonicity of the potential, harmonics and combinations (HCs) transitions are allowed with very small probabilities and can interact with strong natural modes lines via Fermi coupling process and become strong enough to be observed in the natural lines vicinity giving rise to such a fine structure.
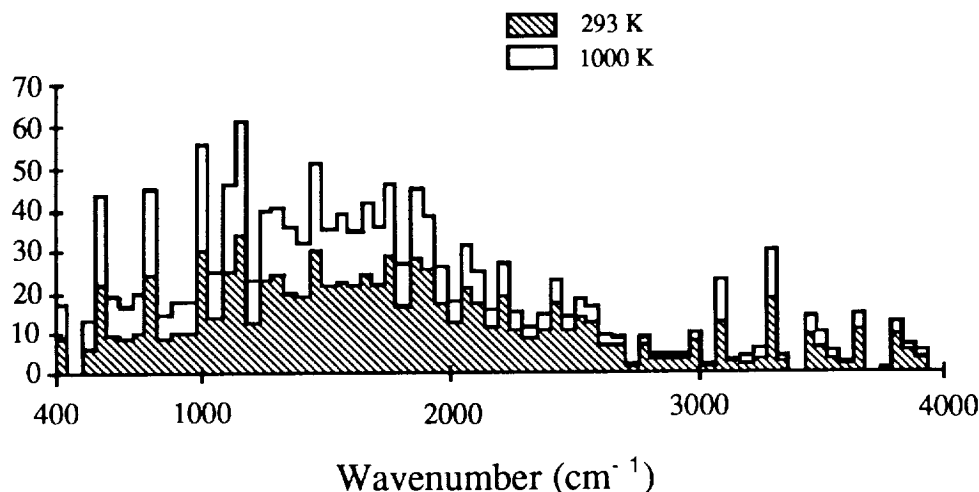
figure n°4 : Histogram in arbitrary units of the density probabilities of the IR active harmonics and mode combinations in the 400 - 4000 cm^{-1} range of wavenumbers for the two extreme temperatures of 300 K and 1000 K.

We have calculated (from the data in ref.2 and 3) the frequencies and symmetry types for all the possible HCs involving two phonons processes issued from the 102 natural modes of the coronene and selected the IR actives ones. A plot of these HCs is presented on fig. n°4. It shows that one cannot explain the continuum observed under the 3.3 μm line in the ISM (a grey body spectrum at $\approx$ 1000 K), by emission from HC lines. Nevertheless, This probability distribution being a priori symmetry group dependent, it as to be investigated for other PAHs of astrophysical interest.

When plotted near the features of the spectrum, it appears that :
- There is no HC in the vicinity of 850 and 545 cm^{-1} which means that it would be difficult to explain the structure of this features with this process.
- On the other hand, there is 17 HCs in the range 2900-3100 cm^{-1}.

So Fermi coupling can explain the 3.3 μm line doubling but not the 11.8 μm and 18.3 μm features structure because there are no candidates for such a coupling.

DIPOLE-DIPOLE INTERACTION

In our sample, there are still some small pieces of coronene crystal. The structure of this crystal is described in ref. 4. We have verified that the shift in frequency due to dipole-dipole interaction is in agreement with the observed spectra in order of magnitude.

For instance, for the 11.9 μm mode which is attributed to the out of plane bending of the C-H bond, the energy interaction between two bonds due to electrical field created by dipoles is $u = d.E = -d^2/R^3$ leading to a force $F_r = d^2/R^4$ where d is the dipolar moment and R the distance of the bonds. Motion equations assuming small amplitudes, gives the shift $\Delta\omega$ from the unperturbed frequency :

$$\frac{\Delta\omega}{\omega} = (1+\frac{4d^2}{kR^5})^{1/2} - 1 \approx \frac{2d^2}{kR^5}.$$

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The shift being very distance dependent, we can only consider the closest bonds couples. Careful examination of the crystal structure shows that these couples are intermolecular ones with $R \approx 1.8$ Å involving approximately one half of the C-H bonds in the crystal. With $d \approx 1$ debye, and $k \approx 0.5 \, r^2 \, 10^5$ dynes/cm where r is the length of an individual C-H bond in Å, one find $\Delta v_{11.9 \, \mu m} \approx 16$ cm^{-1} which is compatible in order of magnitude with the observed shift for this line.

So this effect cannot be ruled out to explain the observed fine structure.

references

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